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Modification of polyethylene terephthalate by atmospheric pressure dielectric barrier discharge (DBD) in view of improving the polymer wetting properties

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Abstract. Surface treatment of polymers by discharge plasmas has increasingly found industrial applications due to its capability of modifying uniformly the surface without changing the material bulk properties. This work deals with surface modification of polyethylene terephthalate (PET) by a dielectric barrier discharge (DBD) at atmospheric pressure. The treatments were conducted in air, nitrogen or argon plasma. The polymer surface was characterized by contact angle measurement, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The results show that the plasma treatment introduces oxygen- and nitrogen- related polar groups on the polymer surface and promotes the surface roughening. Both plasma-induced surface modifications contribute to the enhancement of the polymer wettability.

1. Introduction

Polymers possess good mechanical and chemical properties; however, their use in various applications involving composite and biomaterials, packing, printing, dyeing etc, has been restricted due to their poor adhesion properties. Improvement of the adhesion can be accomplished by chemical methods (adding functional groups on the surface) and/or through introducing micro- or nano-scale roughness on the surfaces. Recently, the classical chemical technologies have been gradually replaced by the environmentally friendly, versatile and low-cost plasma treatment. The atmospheric pressure plasmas are especially attractive as surface modification tools due to their applicability to a variety of substrates, easy scaling-up, quick processing time, and low cost [1].

This work describes the surface modification of a PET polymer by atmospheric pressure dielectric barrier discharge DBD. This type of discharge occurs between two planar or cylindrical electrodes provided that at least one of them is covered by a dielectric layer. As a consequence, after the gas breakdown takes place, the charge accumulation on the dielectric surface prevents the corona-to-arc transition. The DBD plasmas have many applications ranging from surface functionalization and grafting [2], improvement of adhesion and hydrophobicity [3], sterilization [4], processing of textile and fabrics [5] and, most recently, the so-called plasma medicine [6].

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2. Experimental

The experimental arrangement used to create plasma at atmospheric pressure is sketched in figure 1. The DBD discharge was generated between two 9.5-cm-diameter parallel aluminum electrodes fitted in a 150-mm-diameter cylindrical enclosure made of Delrin[®]. A 2.0-mm-thick glass layer completely covered the bottom reactor electrode. The upper electrode was grounded while the lower one was the high-voltage electrode. For all DBD treatments the gas gap was fixed at 3 mm.

Prior to the DBD treatment, the samples (0.5-mm-thick, 10×15 mm²) were ultrasonically cleaned in distilled water, washed in isopropyl alcohol and placed on the lower electrode. The gas flux into the reactor chamber was maintained at 2.4 slm using a rotameter. Three different feeding gases (Air Liquid, Brazil) were used: dry air, argon and nitrogen.

The high-voltage power supply consisted of a step-up high-voltage transformer (110/20000 V, 60 Hz) driven by a Variac autotransformer. The AC voltage applied to the reactor lower plate was measured by a high-voltage probe and displayed on an oscilloscope.

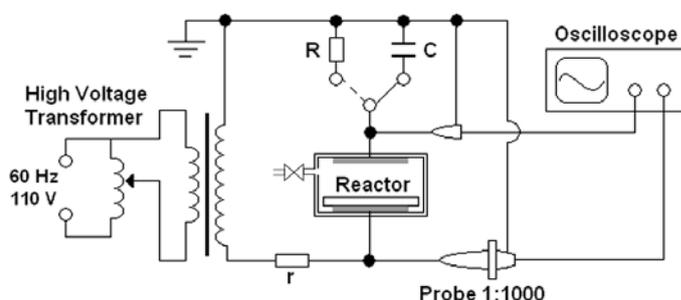


Figure 1. Experimental set-up.

The water contact angle (WCA) was measured by the sessile drop method on a standard Rame-Hart goniometer. The contact angle measurements were made immediately following the plasma treatment and also after some time of storage at controlled ambient conditions (21 °C, and 60 % humidity) to evaluate the stability of the plasma-modified surfaces.

Surface chemical characterization was carried out by X-ray photoelectron spectroscopy using a Kratos XSAM HS system. The spectra obtained were processed by the code provided by the manufacturer using the Shirley method for background subtraction. The value of 284.8 eV of the hydrocarbon C1s core level was used for calibration of the energy scale.

Atomic Force Microscopy–AFM, was used to analyze the surface morphology of the polymer samples. The AFM analysis was performed in air by a Nanoscope–V atomic force microscope. During the analysis, the microscope was operated in tapping mode at a scanning rate of 0.5 Hz.

3. Results and discussion

The DBD discharge operated in filamentary mode and consisted of many tiny streamers distributed over the entire area of the dielectric barrier. The discharge current consisted of a large number of short micro-pulses typical for the DBD discharges. To calculate the charge $Q(t)$ stored on the reactor electrodes, we used a serial capacitor of 0.91 μF . For a DBD driven by an AC power supply, the shape of the Q - V curve (called Lissajous figure) is nearly a parallelogram [7]. The area enclosed by the figure represents the electrical energy consumed for one voltage cycle. The discharge power P is then calculated by multiplying the electrical energy by the frequency of the applied voltage (60 Hz).

Figure 2 shows the Q - V figures of DBD in different gases. As can be seen in figure 2, the shape of the Lissajous figures depends on the feeding gas used. The DBD discharge in Ar was quite unstable and, if operated at voltage with amplitude above 5 kV, turned into arc. Thus, in this case, the DBD voltage was set at 10.0 kVp-p, while the discharge in air and N₂ was operated at 30.0 kVp-p. The mean discharge power measured for the DBD in nitrogen, air and argon gas precursors was 3.3 W, 2.8 W

and 0.9 W, respectively. Since the discharge power in different gas precursors is different, to compare the plasma modification effect the treatment intensity was expressed in terms of the energy density deposited. The DBD treatments at lower power (e.g., in Ar) were conducted for a longer period of time in order to achieve the same energy dose [8], which was set at 13 J/cm². Increasing further the treatment time did not lead to significant changes in the PET contact angle.

Reactions occurring between the plasma species and the polymer chain introduce polar groups on the surface, which results in enhancement of the surface energy and improves the wettability [7, 8]. Immediately after the treatment, the PET samples exhibited WCAs around 50-55°. These values are about 37 % lower than those of the WCA of untreated PET sample (82°). The DBD treatment in N₂ seems to be the most efficient, as resulting in a WCA of about 50°. This finding will be further discussed when presenting the XPS analysis results. It is known that the polymer surfaces treated by plasma and left in ambient conditions tend to recover partially their original wetting properties [9]. This process is referred to as hydrophobic recovery and can be observed in Fig. 3 for the three DBD treatments. The samples treated in air, Ar and N₂ plasmas show similar behavior and, after 3-4 days of storage, the WCA of the PET surface for all DBD treatments reached a saturation value, which was well below than that of the untreated specimen.

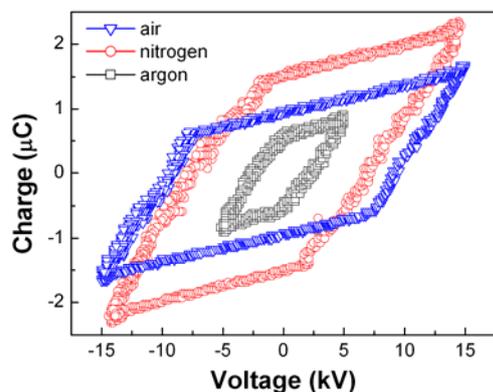


Figure 2. Q-V diagrams for DBD in air, nitrogen and argon.

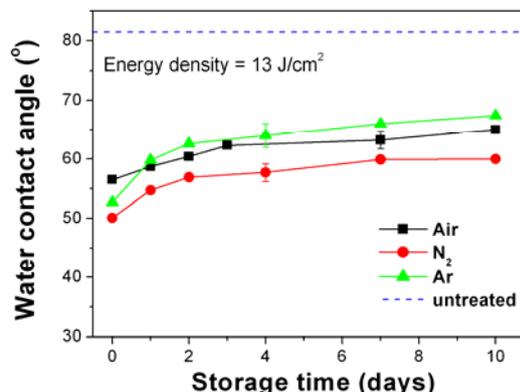


Figure 3. Evolution of water contact angle of plasma-treated PET samples.

The surface atomic composition of the plasma-modified polymers, determined by XPS analysis, is shown in table 1. The measurements were performed 2 weeks after the DBD treatment; therefore, the XPS analysis presents the atomic composition of the saturated polymeric surfaces. As can be seen, all plasma treatments increased the polymer O/C ratio to about the same extent. Since the experiments were conducted in an open environment, it was impossible to ensure a DBD discharge in pure N₂ or Ar atmosphere. Due to residual air trapped in the reactor, oxygen impurities were present in the discharge. This is why the oxygen content on the surface of polymers treated in different discharge gases is about the same. Nevertheless, the O/C ratio is almost the same for the three gases used, while the DBD in N₂ resulted in the highest efficiency in reducing the WCA, as seen in figure 3. This may be explained by the fact that, besides O atoms, the DBD in N₂ also added N atoms to the PET surface (see table 1).

Table 1. Atomic composition of PET samples.

	C (%)	O (%)	N (%)	O/C
Untreated PET	76.1	23.9	-	0.31
Air plasma	70.4	29.6	-	0.42
N ₂ plasma	68.2	28.0	3.8	0.41
Ar plasma	70.8	29.2	-	0.41

To assess the PET surface structural modification, the surface morphology was analyzed by AFM; the results are presented in figure 4. The AFM images show some new nodule-like structures on the treated polymers surface. The size of the structures tends to increase with the treatment time. Formation of similar droplet-like structures, whose sizes depend on the energy dose, was also observed by other authors [9, 10].

Besides oxygen incorporation on the surface through hydrogen abstraction, the plasma reactive species (electrons and UV photons) can also break C-C bonds in the polymer chains producing short polymer segments. Thus, as the treatment proceeds, increasingly lighter oligomers are generated on the surface. These highly oxidized species tend to agglomerate into “bumps”- or “mounds”-like structures on the surface [9]. The formation of these globular shapes can be explained in terms of the difference in the surface energy. The polar and mobile oligomers formed during the plasma exposure would rather prefer to form a cohesive drop instead of spreading on the low-energy polymer surface.

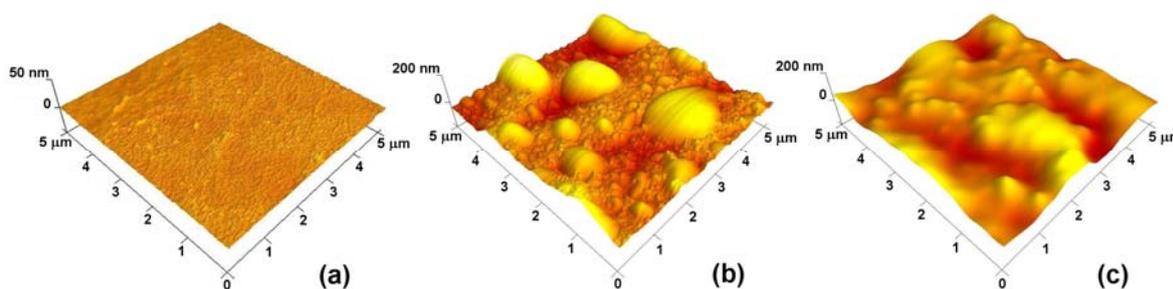


Figure 4. AFM images of PET samples treated in air for a) 0.0 min; b) 5.0 min and c) 10.0 min.

Another factor that influences the material wetting properties is the surface roughness. A hydrophilic surface would have a better wettability as its roughness increases. The roughness values of the plasma-treated PET and a pristine polymer sample are summarized in table 2. As can be seen, the polymers surface roughness increases as a result of the plasma exposure. However, beyond 5 min of treatment the roughness slightly decreased due to excessive surface etching. A similar increase of the polymer roughness was observed in low-pressure plasma treatments of PET and is caused by the formation of nodular structures [10].

Table 2. Surface roughness of PET samples.

	Pristine PET	5-min treated	10-min treated
RMS roughness (nm)	3.68	30.7	25.6

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Conclusions

PET samples were subjected to atmospheric pressure DBD plasma in air, argon and nitrogen. The treatments resulted in incorporation of polar oxygen and nitrogen groups on the PET surface, which enhanced the material’s wetting properties. The DBD process in nitrogen proved to be more efficient probably due to the higher amount of N atoms added to the surface. The polymer surfaces treated in Ar are more likely to undergo hydrophobic recovery. All polymer samples recovered partially their original wetting properties. The plasma treatment resulted also in surface structural modifications and surface roughness enhancement due to surface etching and polymer surface degradation.

Acknowledgment

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